QUALITY ASSURANCE PROJECT PLAN

for the

Virginia River Input Monitoring Program

Prepared by:

Donna L. Belval and Lori A. Sprague U.S. Geological Survey 1730 E. Parham Road Richmond, VA 23228

for Virginia Department of Environmental Quality Chesapeake Bay Office PO Box 10009 Richmond, VA 23240

for the period July 1, 1999 to June 30, 2000

Approvals:	
Lori A. Sprague, Project Manager, USGS	Date
Donna L. Belval, Quality Assurance Officer, USGS	Date
Frederick A. Hoffman, Project Officer, VDEQ	Date
Quality Assurance Officer, VDEQ	Date
Project Officer, US EPA	Date
Ouality Assurance Officer US EPA	 Date

QUALITY ASSURANCE PROJECT PLAN

for the

Virginia River Input Monitoring Program

Prepared by:

Donna L. Belval and Lori A. Sprague
U.S. Geological Survey

for

Virginia Department of Environmental Quality

Chesapeake Bay Office

Richmond, VA

updated June, 1999

TABLE OF CONTENTS

I. PROJECT DESCRIPTION 3
II. PROJECT ORGANIZATION AND RESPONSIBILITY 19
III. QA OBJECTIVES AND CRITERIA 22
IV. SAMPLING PROCEDURES 27
V. SAMPLE CUSTODY 28
VI. CALIBRATION PROCEDURES AND FREQUENCY 29
VII. ANALYTICAL PROCEDURES 30
VIII. DATA REDUCTION, VALIDATION, AND REPORTING 32
IX. INTERNAL QC CHECKS 33
X. PERFORMANCE AND SYSTEM AUDITS 35
XI. PREVENTATIVE MAINTENANCE 36
XII. ASSESSMENT OF DATA VARIABILITY, BIAS, ACCURACY, REPRESENTATIVE NESS, AND COMPLETENESS 37
XIII. CORRECTIVE ACTION FOR OUT-OF-CONTROL SITUATIONS 38
XIV. QA REPORTING PROCEDURES 39

I. PROJECT DESCRIPTION

A. Background

Quantification of the loads of nutrient and suspended solids into the Chesapeake Bay, and evaluation of the trends in constituent concentration are necessary in order to determine the effects that these constituents have on the ecosystems of the Chesapeake Bay. The Virginia River Input Monitoring Program (formerly known as the Virginia Fall Line Nutrient Input Program) was developed to quantify and assess the effectiveness of programs aimed at reducing the impact of nutrient and suspended solid inputs. Load estimates can further be used to calibrate and validate the computer-modeling efforts of the Chesapeake Bay Program.

The U.S. Geological Survey (USGS) began monitoring nutrients and suspended-solids in Virginia in 1984 in cooperation with the Virginia Department of Environmental Quality--Chesapeake Bay Office (VDEQ; at that time, the Virginia Water Control Board) to quantify loads entering Chesapeake Bay from its major tributaries in Virginia. The initial monitoring program consisted of collecting water-quality data on a twice-per-month scheduled basis at sites near the Fall Line on four tributaries to the Bay: the James, Rappahannock, Pamunkey, and Mattaponi Rivers. The Fall Line is geographically defined as the point where the Piedmont Physiographic Province meets the Coastal Plain, and in most instances this corresponds to the point farthest downstream that is unaffected by tides. Loads estimated for rivers at the Fall Line can therefore be used as single-point sources of loads to the Chesapeake Bay.

Loads of nutrients and suspended solids are greatest during stormflow conditions because of higher discharge and often higher constituent concentrations. Therefore, the monitoring program was expanded in 1988 to include more frequent water-quality data collection during stormflow conditions at two major Virginia tributaries to the Chesapeake Bay, the James and Rappahannock Rivers. In July of 1989, the Pamunkey, Mattaponi and Appomattox Rivers were added to this storm-monitoring network. A parallel program has been conducted on 4 tributaries in Maryland by the USGS in cooperation with the Maryland Department of the Environment since 1982.

A seven-parameter log-linear-regression model (Cohn, 1992), which includes variables for discharge, seasonality, and time is used to provide estimates of constituent concentration on days when no concentration data are available. The product of estimated concentrations and daily mean discharge provides daily load estimates, which are then summed to provide monthly and annual loads of selected nutrients and suspended solids. To evaluate long-term change in the input of these constituents, flow-adjusted trends in concentration are computed from the regression model.

B. Objectives and Scope

The Chesapeake Bay River Input Monitoring Program is being used to define the magnitude, timing, and possible sources of nutrient inputs to the Chesapeake Bay from the non-tidal areas of the larger tributaries in Virginia. This sampling program provides a data base of selected constituents (nutrients and suspended solids) for periods of varying flow and season, which are used to produce estimates of constituent loading to the Chesapeake Bay.

The specific objectives of this program are to:

- (1) describe concentrations of selected nutrients and suspended solids in terms of flow and season for five major tributaries to the Chesapeake Bay in Virginia near the Fall Line,
- (2) compute monthly and annual loads of nutrients and suspended solids,
- (3) compare concentration data and load estimates between rivers,
- (4) compute trends in nutrient and suspended solid loads over time,
- (5) explain possible factors influencing concentration, loads, and trends of nutrients and suspended solids,
- (6) assess quality-assurance results in order to describe the quality of the analyses provided by the participating laboratories, and
- (7) provide information needed to refine the network design for future monitoring programs for the Chesapeake Bay.

The stations monitored and their station numbers include:

(1) the James River at Cartersville
USGS 02035000, VDEQ TF5.1
(2) the Rappahannock River near Fredericksburg
USGS 01668000, VDEQ TF3.1
(3) the Appomattox River at Matoaca
USGS 02041650, VDEQ TF5.4A
(4) the Pamunkey River near Hanover
USGS 01673000, VDEQ TF4.1
(5) the Mattaponi River near Beulahville
USGS 01674500, VDEQ TF4.3

Water-quality sample collection began July 1, 1988, for the James and the Rappahannock Rivers, and July 1, 1989, for the Appomattox, Pamunkey, and Mattaponi Rivers. Samples are collected on a twice-per-month scheduled basis, which most often occurs during baseflow conditions. These samples are collected by both USGS and VDEQ personnel at the James, Pamunkey, and Mattaponi Rivers. Samples also are collected during stormflow conditions, in order to cover a range in flow conditions. Storm samples at all stations, and baseflow samples at the Appomattox and Rappahannock Rivers, are sampled exclusively by USGS personnel. Monthly and annual loads of selected constituents are estimated using a seven-parameter log-linear-regression model (Cohn, 1992).

C. Data Usage

The data collected for the Virginia River Input Monitoring Program are used to help define the magnitude, timing, and sources of nutrient inputs to the Chesapeake Bay from the non-tidal areas of the five major tributaries in Virginia. Additionally, this information can help gauge the success of management practices aimed at reducing these inputs. These data provide a data base of selected nutrients and suspended solids collected during periods of varying flow and season, which are being used to estimate loads to the Chesapeake Bay of the selected constituents.

Concentration data and statistics from the concentration data will be used to describe the water-quality characteristics of each river, including concentration ranges and medians; the relations between concentration and discharge; and concentration and seasonality at each river. The load estimates will be compared to the loads from other rivers in the Chesapeake Bay, in order to see the relative differences between the basins. Differences may be examined using land-use information, discharge records, and possibly point and nonpoint sources of constituents. Trend estimates will be used to determine the changes in constituent inputs over the period of study, and to assess the impact of management practices implemented during that time.

Historical data may be used as background information for comparison purposes. Quality assurance data are used on an ongoing basis to evaluate field and analytical methods for representativeness, variance, bias, and accuracy.

D. Study Design and Rationale

The contributing basins for this report together comprise about 22 percent of the total Chesapeake Bay drainage area. The James and Rappahannock River basins represent approximately 13 and 4 percent of the Chesapeake Bay drainage area; the Appomattox, part of the lower James River Basin, represents another 2.5 percent; and the Pamunkey and Mattaponi River basins represent about 2 and 1 percent of the total Chesapeake Bay drainage area. The remaining percentage of Virginia within the Chesapeake Bay watershed is comprised of the Potomac River basin and its tributaries including the Shenandoah River, which are monitored by the Maryland District of the USGS, and are not included in this plan.

Table 1 presents the basin size, the percent land use in the Chesapeake Bay watershed, the percent land use in Virginia and the percent land use within each of the basins monitored for this report. The locations of the five river basins and the River Input monitoring stations are shown in Figure 1. A description of each river basin and each sampling station follows. The rivers are referred to throughout this report in order by decreasing drainage area of each basin.

Table 1. Land use for the Chesapeake Bay, the Chesapeake Bay watershed in Virginia, and selected riverbasins in Virginia

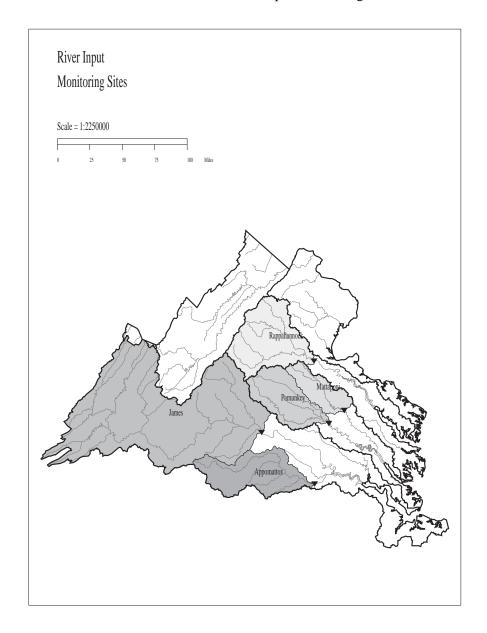
 $[m \ \hat{r}]$, square m iles \times , less than] (Neum iller and others, 1995; Chesapeake Bay Program, written commun., 1994)

Geographic area	Drainage Area (m i²)	Urban (percent)	Agricultural (Herbaceous) (percent)	a/ Forested (W oody) (percent)	W ater (percent)	<u>b</u> /Total (percent)
Chesapeake Bay	64,000	8	33	58	1	100
Virginia	40,815	10	31	58	1	100
James River Basin	10,206	8	25	65	1	99
Rappahannock River Basin	2,848	6	40	54	<1	100
Appomattox River Basin	1,600	3	33	61	<1	98
Pamunkey River Basin	1,474	3	35	59	2	99
Mattaponi River Basin	911	2	27	69	<1	99

 $[\]underline{a}$ Includes wetlands.

 $[\]frac{b}{}$ Total percentage below 100 percent is possibly due to rounding and inaccuracies in area estimates.

Figure 1. Location of the five river basins and the River Input Monitoring Stations.



The area of the James River Basin is approximately 10,206 mi², or about one-fourth of the area of Virginia, and is the third largest source of freshwater to the Chesapeake Bay, after the Susquehanna and Potomac Rivers. The James River Basin extends from the eastern part of West Virginia through four physiographic provinces (1) Valley and Ridge, (2) Blue Ridge, (3) Piedmont, and (4) Coastal Plain. The major cities in the James River Basin include Richmond, Lynchburg, Petersburg, Charlottesville, Williamsburg, Hopewell, and parts of Norfolk and Newport News.

The water-quality monitoring station at the James River near Cartersville, Va. (USGS station 02035000 and VDEQ station TF5.1), represents the contributing area (6,257 mi²) to the Chesapeake Bay from Virginia near the Fall Line, or about 60 percent of the James River Basin drainage area. This station is about 40 mi upstream of the Fall Line, but was selected because of the well-documented long-term flow record, and because there are no major streams contributing to the flow between this station and the Fall Line at Richmond. Because of the size of the basin upstream of the sampling station, streamflow varies widely, depending on precipitation patterns which may result in either very localized or widespread stormflow events. The average discharge at this site, computed during a period of 94 years, is 7,077 ft³/s (Prugh and others, 1994). The location of this monitoring site is lat 37°40'15", long 78°05'10", which is at State Highway 45 at the Goochland/Cumberland County line, Va.

The Rappahannock River Basin encompasses a land area of approximately 2,848 mi² which constitutes about 7 percent of the State of Virginia. The river flows from the eastern edge of the Blue Ridge physiographic province through the rolling hills of the Piedmont and Coastal Plain to the Chesapeake Bay, and is the second largest contributor of flow to the Chesapeake Bay from Virginia. The major cities or towns in the basin include Fredericksburg, Warrenton, Winchester, Culpeper, and Orange.

The Rappahannock River monitoring station (USGS station 01668000) is located upstream of Fredericksburg, Va. (This USGS station is at a cableway located 2.8 miles upstream of a VDEQ station (TF3.1) at the Route-1 bridge; data from the VDEQ station is not used in this study). The station is inaccessible during extreme high-flow events; therefore, stormflow samples are collected at those times from the Interstate-95 bridge located 0.9 miles downstream of the station. There are no major contributors of flow to the river between these two points. The area of the drainage basin upstream from the sampling station is approximately 1,596 mi², which is about 56 percent of the Rappahannock River basin. Upstream from this station, most of the basin is in the uplands of the Piedmont Province, and because of the high relief, the river produces rapid or "flashy" streamflow peaks as a result of precipitation. The river therefore may carry large loads of suspended solids and other constituents relative to the size of the basin. The agricultural land use in the basin and expansion of the Washington, D.C., suburbs may increasingly affect the water quality of the river by causing elevated sediment concentrations in runoff, and an increase in concentrations of nutrients associated with the sediment, such as total phosphorus. The average discharge at this station is 1,660 ft³/s, computed during a period of 86 years (Prugh and others, 1994). The location of the sites in Spotsylvania County, Va., are: lat 38°19'20", long 77°31'05" for the USGS station and lat 38°19'36", long 77°30'08" for the I-95 bridge, and lat 38°19'12", long 77°28'18" for the Rt-1 bridge.

The Appomattox River Basin is within the James River basin, but because the Appomattox River enters the James River below the Fall Line, it is not included as a source to the James River monitoring station at Cartersville, and so is monitored separately. The basin area above the confluence with the James is 1,600 mi², approximately 16 percent of the James River basin and 4 percent of the area of Virginia. The Appomattox River basin begins in the Piedmont physiographic province, and flows through a small portion of the Coastal Plain before it flows into the James River near Hopewell. The Appomattox River basin is primarily rural, although the cities of Petersburg, Colonial Heights, and Hopewell are within the basin, downstream of the sampling station at Matoaca.

The drainage area of the Appomattox River basin above the sampling station at Matoaca (USGS station 02041650) is approximately 1,344 mi². The monitoring station is unique among the River Input Monitoring stations in that the flow is controlled by a dam at Lake Chesdin, 2.8 miles upstream of the sampling station. This tends to delay water-level rise from storms, so that the water level is very slow to rise and to fall in comparison to the other monitoring stations. Downstream of Lake Chesdin, the steep gradient due to the rapid elevation change, and a streambed of rocks and boulders result in expanses of rapids between the dam and the sampling station. The average discharge at this station is 1,384 ft³/s, computed during a period of 23 years (Prugh and others, 1994). The location of the site in Chesterfield County is lat 37°13' 28", long 77°28' 32".

The total area of the York River Basin is approximately 2,650 mi², about 6.5 percent of Virginia's total land area, consisting of the Pamunkey River, the Mattaponi River, and the coastal area below the sampling stations. Agriculture is an important component of the economy of the York River basin, and the area is primarily rural. Although the Pamunkey and Mattaponi Rivers are often collectively presented as the York and have many similarities, each river has unique basin, flow and water-quality characteristics. The Pamunkey and Mattaponi River basins are monitored above their confluence to form the York, and are reported separately for this study.

The total area of the Pamunkey River Basin is 1,474 mi², or about 4 percent of Virginia. The Pamunkey River basin begins in the lower part of the Piedmont Province where the relief is relatively low and extends into the Coastal Plain. The basin contains expanses of forested wetlands and marshes that are significant sources of wildlife productivity (Virginia Water Control Board, 1988). Ashland and Mechanicsville are the two major towns in the basin.

The Pamunkey River basin monitoring station (USGS station 01673000 and VDEQ station TF4.1) is located near Hanover, Va. The area of the drainage basin above the sampling station is approximately 1,081 mi², which is about 40 percent of the York River basin. The low relief and relatively wide basin tend to produce stormflow peaks that are slow to peak and to recede. There is some regulation of the Pamunkey River from the dam at Lake Anna, approximately 100 mi upstream of the monitoring station, on the North Anna River. The average discharge at this station is 1,110 ft³/s, computed during a period of 21 years (Prugh and others, 1994). The location of the site in Hanover County, Va., is lat 37°46′03″, long 77°19′57″.

The Mattaponi River basin is 911 mi², or two percent of the area of Virginia, and also is located within both the Piedmont and Coastal Plain physiographic provinces. Like the Pamunkey River, it tends to have expanses of wetland areas (VWCB, 1991). The wetland areas tend to slow flow velocities, and the hydrographs during storms are slower to peak and recede than at the Pamunkey River.

The Mattaponi River monitoring station (USGS station 01674500 and VDEQ station TF4.3) is located near Beulahville, Va. The area of the drainage basin above the sampling station is approximately 601 mi², which is about 23 percent of the entire York River basin, and two percent of the area of Virginia. Like the Pamunkey, the Mattaponi River basin has expanses of freshwater wetlands (VWCB, 1991). The average discharge at this station is 583 ft³/s, computed during a period of 50 years (Prugh and others, 1994). The location of the site in King and Queen County is lat 37°53′ 02″, long77°09′ 55″.

All 5 monitoring stations were part of the USGS National Stream Quality Accounting Network (NASQAN) from the mid 1970's through 1992. NASQAN was a nationwide long-term water-quality sampling network, designed for long-term data collection and analysis. The NASQAN data serve as historic background data for these stations, and may be of use in interpretation of the River Input data in the future.

E. Description of Streamflow

Constituent concentrations within a river change as a function of streamflow. In addition, streamflow data is necessary to compute constituent loads. An overview of the streamflow conditions at all five stations is shown in Table 2. Table 2 gives information on the central values of the streamflow (mean and median) as well as the extremes. The monthly mean discharge is computed by averaging the daily mean discharges in each month. The normal range of monthly discharge is the range of flows that could be expected for any individual month and represents flow conditions that are not considered exceptionally high or low. The normal range for a specific month is calculated by ranking all monthly mean discharge values for that month during (over) the period of streamflow record. The 25th percentile, or that flow which is exceeded by 75 percent of the monthly mean discharges, and the 75th percentile, or that flow which is exceeded by 25 percent of the monthly mean discharges, are then determined. The normal range is the range in discharge between these two values. Historically, the monthly mean discharge is in the normal range 50 percent of the time.

Table 2.D rainage area, historic stream flow conditions, and stream flow conditions for the period of study for the R iver Inputm on itoring stations in V irginia $[mi^2$, square miles; ft^3/s , cubic feet per second; ft/s, feet per second; --,not applicable]

Tin e period	Drainage areamí²	Mean discharge (ft.3/s)	Median discharge (ft ³ /s)	Maximum Instantan- eous discharge (ft ³ /s)	Minimum Instantan- eous discharge (ft ³ /s)
			James River		
Period of record	6,257	7,154	4,460	362,000	316
July 1988-September 1997	-	7,727	4,900	158,000	801
		Ra	ppahannock Ri	<u>iver</u>	
Period of record	1,596	1,685	984	140,000	5.0
July 1988-September 1997	-	1,893	1,050	74,100	101
		<u> </u>	Appomattox Ri	<u>ver</u>	
Period of record	1,344	1,387	695	40,800	26
July 1989-September 1997	-	1,228	657	12,500	26
		I	Pamunkey Rive	<u>er</u>	
Period of record	1,081	1,142	620	29,900	47
July 1989-September 1997	-	1,083	544	21,200	47
			Mattaponi Riv	<u>er</u>	
Period of record	601	588	374	16,900	5.9
September 1989-September 1997	-	568	251	7,910	6.3

F. Monitoring Parameters and Frequency of Collection

Table 3 shows the constituents monitored for this study, the detection limits at each laboratory, and the reference to the method used.

Samples are analyzed for the following constituents:

<u>Nitrogen species</u> --particulate nitrogen, total dissolved nitrogen, dissolved ammonia nitrogen, dissolved nitrite, dissolved nitrate. (Prior to February 1996, total Kjeldahl nitrogen - ammonia plus organic species - was also determined). The concentration of dissolved nitrite-plus-nitrate nitrogen is the sum of dissolved nitrite concentration and dissolved nitrate concentration.

<u>Phosphorus species</u> --particulate phosphorous, total dissolved phosphorous, dissolved orthophosphorus. (Prior to February 1996, total phosphorus was also determined). <u>Other species</u> -- dissolved silica, total suspended solids

Approximately 40 stormflow samples per year were initially needed to accurately estimate loads using the log-linear regression model selected for this study, so that stormflow-sampling criteria were established by determining a gage height that is reached at each river about 40 times per year. At progressively higher gage heights, the water level would be reached on a fewer number of days. Emphasis was placed on sampling throughout the range in storm conditions that existed throughout the sampling period. Although sampling criteria remain the same, currently only 20 storm samples per year are needed to accurately estimate loads using the log-linear regression model selected for this study and utilizing the data previously collected for this project.

The specific sampling criteria are listed in Appendix 1. These criteria are used as guidelines for sample collection, and are not strict criteria. During extreme low-flow or high-flow periods, the sampling criteria can be modified in an attempt to obtain the target number of samples. Whenever possible, and as permitted by discharge conditions, water samples are collected during the rise, peak, and fall of the stormflow hydrograph.

Appendix 2 shows an example of the record of field data planned, including quality assurance data. This form is also used by field personnel to document that the sample was collected. This record is kept for each of the 5 stations.

In order to objectively define whether a sample was collected at base flow or stormflow, hydrographs are separated into two components, stormflow and base flow, to determine the contribution of stormflow and base flow to the total annual flow (White and Sloto, 1990.) Hydrograph separations are performed using the local minima technique as described by Pettyjohn and Henning (1979). Samples are determined to be baseflow or stormflow samples based on model output.

Table 3. Virginia River Input Monitoring Program Detection Limits

Table 3.

Analyte	NWIS Code/ Storet Code	VDCLS Analytical Method	Detection Limit ^{1/}	VDCLS Parameter Group	VDCLS Catalog Number	VDCLS Group Description	
Total Dissolved Nitrogen	00602/ 00602	Colorimetric, Chesapeake Bay (D'Elia ^{2/})			190-263	Nutrients CBM	
Dissolved Ammo- nia Nitrogen	00608/ 00608	EPA 350.1	.004 ppm			Field Filtered Vol.req 1 qt.	
Dissolved Nitrate	00618/ 00618	EPA 353.2	.004 ppm				
Dissolved Nitrite	00613/ 00613	EPA 353.2	.002 ppm				
Total Dissolved Phosphorus	00666/ 49572	Colorimetric, Chesa- peake Bay (D'Elia)	.001 ppm				
Dissolved Orthophosphorus	00671/ 00671	EPA 365.1	.002 ppm				
Dissolved Silica	00955/ 00955	Standard Methods 4500-Si F (17th Ed.)	.1 ppm				
Particulate Nitrogen	00601/ 49570	EPA 440.0	.001 ppm	P-BNUT	190-270	Nutrients CBM Vol.req. 1 qt	
Particulate Phosphorus	00667/ 49567	Colorimetric, Chesa- peake Bay (Aspila ^{3/})	.0001 ppm				
Total Suspended Solids	00530/ 00530	Standard Methods 2540 D (17th Ed.)	3 mg/L	P-NME7	190-021	Non-Metal Analysis Vol. req. 1 gal	
Volatile Suspended Solids	00535/ 00535	Standard Methods 2540 D (17th Ed.)	3 mg/L				
Fixed Suspended Solids	00540/ 00540	Standard Methods 2540 D (17th Ed.)	3 mg/L				
Turbidity	00076/ 00076	EPA 180.1	0.01 NTU				

½ Detection limits are determined on a yearly basis by VDCLS, using the procedure found in Appendix B of EPA CFR Part 136.

²/_D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples Using Persulfate Digestion. Limnol. Oceanogr. 22:760-764.

^{3/} Aspila, Agemian and Chau, 1976. A semi-automated method for the determination of inorganic, organic, and total phosphate in sediments. Analyst 101:187-197.

II. PROJECT ORGANIZATION AND RESPONSIBILITY

The organization of the project for the Virginia River Input Monitoring Program is outlined in the diagram below. The duties of the individuals are also described below.

Project Officer Frederick Hoffman Chesapeake Bay Office/ VDEQ 804-698-4334 Fax 804-698-4319

Principal Investigator
Lori Sprague
U.S. Geological Survey, WRD
*804-261-2635
*Fax 804-261-2659

Field Sampling	<u>Laboratory</u> <u>Analysis</u>	Data Management	<u>Data Analysis</u>
USGS *Hydrologic Techni-	VDCLS Sherry Lacy	USGS	USGS
cians and Hydrologists as needed	804-786-4853 (Nutrients) Bertie O'Neal 804-786-7748 (Solids)	*Hydrologist (2) Hydrologic Technician	*Hydrologist (3)
VDEQ Richmond, VA	USGS	VDEQ	USGS, Baltimore, MD
Mark Alling	NWQL	Cindy Johnson	Hydrologist
804-527-5021	303-467-8000	804-698-4385	410-238-4200

^{*}same phone and fax numbers as above

VDEQ, Virginia Department of Environmental Quality, Richmond, VA; USGS, U.S. Geological Survey; VDCLS, Virginia Division of Consolidated Laboratory Services, Richmond, VA; NWQL, USGS National Water Quality Laboratory, Arvada, CO **PROJECT OFFICER**

Frederick Hoffman

Virginia Department of Environmental Quality

Box 10009

Richmond, VA

804-698-4335

Fax 804-698-4319

Responsible for overseeing the administrative aspects of the program including fiscal

management, coordination among other administrators, and coordination with cooperating

agencies and institutions. Approves technical design, conduct, and data analysis of the program.

PRINCIPAL INVESTIGATOR

Lori Sprague

U.S. Geological Survey, WRD

1730 East Parham Road

Richmond, VA 23228

804-261-2635

Fax 804-261-2659

Responsible for the technical design, conduct, and data analysis of the program. Provides guidance

to other key personnel and directs the efforts to organize, describe, and interpret the results of the

monitoring. Has ultimate responsibility for quality assurance.

FIELD SAMPLING

Supervisory Hydrologic Technician, U.S. Geological Survey, Richmond, VA

Hydrologic Technician(s), U.S. Geological Survey, Richmond, VA

Other Hydrologists and Hydrologic Technicians as needed

Coordinate all field activities of the program, including procuring all necessary equipment,

collecting water samples according to the USGS sampling protocol, measuring field parameters,

and coordinating all field quality assurance data collection.

21

LABORATORY ANALYSIS

Virginia Division of Consolidated Laboratories (VDCLS), Richmond, VA

Sherry Lacy - Nutrients Bertie O'Neal - Solids, Carbon

Complete laboratory analyses on a timely basis and return analytical results to VDEQ-CBO.

Provide assistance with information concerning analytical techniques for constituents.

USGS National Water Quality Laboratory (NWQL), Arvada, CO

John Vasquez, Supervisory Chemist - Nutrients Harold Ardourel, Supervisory Chemist - Solids

Analyzes laboratory-split samples for quality-assurance purposes. Provides standard-reference samples to VDCLS.

DATA MANAGEMENT

Hydrologist(s), U.S. Geological Survey, Richmond, VA Hydrologic Technician, U.S. Geological Survey, Richmond, VA

Cindy Johnson, Virginia Department of Environmental Quality, Richmond, VA

Responsible for maintaining the Virginia data base and transferring and checking all data from VDCLS to the USGS. Responsible for facilitating the transfer, collation, and retrieval of the data. Responsible for quarterly progress reports to VDEQ.

DATA INTERPRETATION

Hydrologist(s), U.S. Geological Survey, Richmond, VA Hydrologist, U.S. Geological Survey, Baltimore, MD

Responsible for graphing, presentation and interpretation of the data; application of quality assurance data; and all formal report requirements for the program.

III. QA OBJECTIVES AND CRITERIA

Because data collected for the Virginia River Input Monitoring Program are used to (1) help define the magnitude and timing of nutrient inputs to the Chesapeake Bay at the Fall Line and (2) to provide a data base of selected constituents collected during periods of varying flow and season, several general quality assurance objectives are necessary in order for the program to be successful.

A. Comparability of Results

The data collected for this program must be comparable and reproducible. Therefore, sampling methods and sample analyses must be uniform and consistent among the agencies collecting and analyzing the data. This plan includes (1) a field component to assure that water quality samples are representative of river conditions and (2) a laboratory component to assess the variance, accuracy, and bias of analytical results.

The field component consists of documentation of field conditions, collection procedures, and equipment as follows:

(1) Water quality samples are collected using approved USGS guidelines to ensure the collection of samples that are representative of the river cross-section. These guidelines assure the collection of a representative, composite sample from the horizontal and vertical cross section of the river. To ensure the collection of representative samples, an analysis of historic cross-sectional variability of conductance, water temperature, dissolved oxygen, pH, and suspended sediment was used to determine that the sampling points across each river adequately represented the vertical and horizontal water-quality conditions within the cross section.

- (2) Sampling criteria based on flow characteristics are documented for field personnel (Appendix 1) to ensure that water-quality samples are collected over a range in flow conditions. In addition, detailed recording of field procedures ensures consistency of procedures between field personnel.
- (3) Proper use of sampling and monitoring equipment and sample collection techniques by field personnel is verified with in-house testing of field procedures through a twice-per-year National Field Quality Assurance Program.
- (4) Proper cleaning procedures of sampling equipment is documented through ongoing comparisons of field blanks, scheduled as in Appendix 2.

The laboratory component of this plan consists of the collection and analysis of duplicate, laboratory-split, and standard-reference samples as follows, and as scheduled in Appendix 2:

- (1) Duplicate samples are used to document the variance of the analytical results.

 Duplicate samples are prepared by withdrawing two subsamples of the full sample volume collected. Both samples are then analyzed by VDCLS. The second subsample is disguised as an environmental sample by labeling it with a different time from the first subsample.
- (2) Laboratory-split samples are used to document bias in the analytical results.

 Laboratory-split samples are collected in a similar manner to duplicate samples; however, one subsample is analyzed by VDCLS and the other subsample is analyzed by NWQL.

 The results are used to assess the comparability of results between the two laboratories and to determine any bias.
- (3) Standard-reference samples document the ability of a laboratory to accurately analyze samples of known concentrations and to check for bias in analytical results. Standard-reference samples are prepared in the USGS laboratory and submitted to VDCLS and NWQL for analysis.

In addition to the field and laboratory components of the quality assurance plan, there is also inhouse checking of data that are received from the laboratory. All data are logged in as they arrive from VDCLS, then later are reviewed for transcription errors and corrected.

Concentrations below the minimum reporting limit ("censored" data) are considered in the regression model to be equal to the minimum reporting limit as long as fewer than 25 percent of the data are censored. The adjusted maximum likelihood estimator (AMLE) is used in the few cases where censoring is greater than 25 percent (Helsel and Cohn, 1988). In summations of total nitrogen and total phosphorus from their respective dissolved and particulate constituents, the sum is taken to be a value less than the combined minimum reporting limits if both the particulate and dissolved values are censored ($\langle V_1 + \langle V_2 = \langle (V_1 + V_2) \rangle$). If just one value is censored, the sum is considered to be the uncensored value plus half the minimum reporting limit for the censored value ($\langle V_1 + V_2 = 0.5V_1 + V_2 \rangle$).

Calculations for all duplicate data are also performed with the censored data equal to zero in order to define the range of variance for each constituent. Concentrations that appear to be outliers are reexamined, using the field notes to determine the presence of any unusual circumstances or hydrologic conditions. If there is no indication of anything out-of-the-ordinary, the laboratory is asked to review their records for accuracy. If necessary, data are corrected and changes are documented with the rationale and source of changes made.

B. Completeness of Sampling

A complete data set is needed to meet the objectives of the project. In particular, the suites of analyses must be comprehensive, and the sampling coverage must capture the variability of both base-flow and high-flow instantaneous loadings of the constituents. Completeness is documented by:

- 1. Periodic checks by the project water-quality data base manager which assess the completeness and accuracy of calculations for the analyses.
- Assessment of the number of samples collected versus the number of samples received.
 An ongoing list is kept to make sure that all analyses are received from VDCLS.
 Periodically, this list is sent to VDCLS and VDEQ, for their information and use.
- 3. Development of as complete and representative a data set as possible, covering all streamflow conditions, using the criteria documented in Appendix 1.
- 4. Collection of field and quality-assurance data on a scheduled basis, with documentation of each sample as shown in Appendix 2.

C. Representativeness

The collection of water-quality samples representative of river conditions is essential. Samples therefore are collected using approved USGS protocols for water-quality sampling, ensuring that water-quality conditions are represented as closely as possible.

Water-quality samples are collected by both VDEQ and USGS during baseflow and by the USGS during stormflow using an equal-discharge increment (EDI) method or an equal-width increment (EWI) method, so that a sample representative of stream conditions is obtained. The EDI method, in which samples are obtained at the centroids of equal discharge increments, is normally used in streams with stable channels where discharge ratings change very little during the year. The EWI method, in which samples are collected at centroids of equal-width increments of the stream, is used most often in shallow or sandbed streams where the distribution of water discharge in the cross-section is not stable, or in streams where the distribution of discharge in the cross-section is unknown. Samples are collected using a USGS-designed depth-integrating sampler (designation D-74 or D-74AL) when average streamflow velocities exceed 1.5 ft/s, or a weighted sample bottle at lower velocities when depth-integrating samplers are not effective. A depth-integrating sampler is designed to sample the vertical water column of the river proportionally to the velocity at each depth. These methods are documented by Edwards and Glysson (1988) and Ward and Harr (1990). Sampling equipment specific to each station is documented in Appendix 3.

All samples collected at the James River station, the Mattaponi River station, and the Appomattox River station by USGS personnel are collected by the EDI method. All samples at the Rappahannock River station are collected by USGS personnel using the EDI method, except samples collected from the I-95 bridge during extreme events, when an EWI method is used. All samples at the Pamunkey River station are collected using an EWI method. Monthly scheduled samples collected by the VDEQ at the James, Pamunkey, and Mattaponi River stations are collected using a point sampler at approximately equal-width increments across the river.

VDEQ personnel did not have access to a depth-integrating sampler; therefore, only those VDEQ samples collected when stream velocities are less than 1.5 ft/s, when point samplers would be effective according to USGS procedures, are used in this study.

IV. SAMPLING PROCEDURES

Water-quality samples are collected according to established U.S. Geological Survey sampling protocol for nutrients and suspended solids. These methods are documented in the publications *Field methods for measurement of fluvial sediment*, by T.K. Edwards and D.G. Glysson, 1988; U.S. Geological Survey Open-File Report 86-531, in *Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses*, by J.R. Ward and Albert Harr, 1990, U.S. Geological Survey Open-File Report 90-140; and in *U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water*, by A.J. Horowitz and others, 1994, U.S. Geological Survey Open-File Report 94-539.

Samples are collected in a manner ensuring that they are representative of river conditions, which involves collecting horizontally and vertically integrated samples. Sampling equipment is made from non-contaminating materials, which includes epoxy-coated depth integrated samplers for collection of the nutrients and suspended solids samples. Nutrients samples are filtered in the field using an in-line, 0.45 um Gelman capsule filter. All samples are preserved on ice and taken to VDCLS on the same day if possible, or as soon as feasible. (NOTE: Samples prior to January 15, 1994, were filtered in the VDCLS laboratory. After that date, field filtering using the Gelman filter was instituted as part of the procedure.)

Because of variations in flow conditions, width of each streambed, and differences in cross-sectional morphology, sampling procedures between the five rivers differ. Protocols were developed for each site, outlining where samples are to be taken in the cross section, what type and size of sampler to use, how samples are to be labeled, and the number of samples to collect, in order to ensure that all personnel responsible for sampling use the correct procedures. The protocols are attached as Appendix 4.

V. SAMPLE CUSTODY

Collected water samples are packed in ice and transported to VDCLS. A VDCLS laboratory analysis request form (Appendix 5) is sent with each sample shipment, detailing the analyses to be performed on the samples. Additionally, a Virginia District field form is completed and kept on file in the Virginia District Office as a record of the samples collected, to check for final completeness of the analyses, and to record field measurements, date and time of collection, and any unusual conditions. When laboratory split samples are collected, the NWQL analysis request form is also completed, to be sent with the samples to NWQL.

Samples are collected in 1-liter plastic "cubitainers" provided by VDCLS through the Chesapeake Bay Office of VDEQ, labeled using a VDCLS tag, immediately put on ice and transported to the VDCLS laboratory. No other preservation is necessary. At those times when it is impossible to take samples to the laboratory, samples are refrigerated at 4° C and taken to the laboratory as soon as possible. Samples are delivered with laboratory analysis request forms, which include field measurements and documentation of date and time for each sample.

Laboratory-split samples for quality assurance are sent to the USGS National Water Quality
Laboratory (NWQL) in Arvada, Colorado and are collected in bottles provided by the NWQL.

Quality assurance of materials used in the containment and preservation of water samples for

NWQL is performed by NWQL. As soon as possible after field collection, samples are shipped on
ice to the laboratory. An NWQL laboratory analytical services request form (Appendix 6) is sent
with each sample shipment, which details the analyses to be performed on the samples.

Additionally, a field sheet (Appendix 7) which details field conditions and field parameter values
is completed for each sampling trip and kept in the office along with a copy of the analytical
services request form. (NOTE: Use of sulfuric acid as a preservative for filtered nutrient samples
sent to NWQL will begin in January 1999.)

VI. CALIBRATION PROCEDURES AND FREQUENCY

Calibrations are made on pH meters, specific conductance meters, and dissolved oxygen meters in the field before each use. A separate equipment calibration log is kept with each of these meters in the field vehicle. These logs record the date, results of the calibration, identification of standards, initials of field person, and any corrective actions taken. Both pH and specific conductance standards are supplied by the USGS laboratory in Ocala, Florida; each standard has expiration dates posted on its container.

Calibration of laboratory equipment at VDCLS is documented in the publications entitled *Quality* Assurance Plan for the Virginia Division of Consolidated Laboratory Services, 1982, and Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982.

Calibration of laboratory equipment at NWQL is documented in the publications entitled *Quality* Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982; and in Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, M.J. Fishman and L.C. Friedman: Open-file report 85-495, Denver, 1985.

VII. ANALYTICAL PROCEDURES

The majority of samples collected are analyzed by VDCLS. Selected quality-assurance samples are analyzed by either VDCLS or the USGS National Water Quality Laboratory (NWQL) in Arvada, CO. Samples collected prior to January 15, 1994 were filtered and analyzed by VDCLS under criteria established by Clesceri, Greenberg, and Trussell (1989) and the USEPA Environmental Monitoring and Support Laboratory (1983). Beginning January 15, 1994, samples have been filtered in the field using procedures established by Horowitz and others (1994) before being delivered to the laboratory for analysis.

Requirements set by the USEPA for regulatory laboratories state that nutrient samples be filtered within 24 hours and suspended-solids determinations be performed within 7 days. Samples collected on weekends are chilled to 4°C and held until they can be accepted by VDCLS the following week. Approximately one of every ten samples is sent to both VDCLS and NWQL as a quality assurance check of the analytical results. Samples sent to NWQL are filtered and preserved in the field by chilling, then shipped by express mail to the laboratory. The analyses are performed within 7 days after receipt at the laboratory. Analytical methods used at NWQL are documented in Fishman and Friedman (1989).

NWQL performs selected quality assurance analyses of water collected at the five Chesapeake Bay River Input Monitoring stations. The analytical procedures used by the laboratory are standard for use in water quality studies, and are documented in the publication entitled, *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, Book 5, Chapter A1, M.J. Fishman and L.C. Friedman, Open-file report 85-495, Denver, 1985.

In some instances, the analytical method for certain constituents differs for the total constituent and the dissolved constituent. For each analytical method there is a range within which the actual concentration is expected, so that it is possible for the analytical result of the total concentration of a particular constituent to be less than that of the dissolved concentration for that constituent. Minimum reported concentrations may differ according to the detection limit, depending on the specific technique done by the laboratory.

The concentration of total nitrogen for this project is computed as the sum of particulate nitrogen and dissolved nitrogen for VDCLS samples and as the sum of dissolved nitrite-plus-nitrate nitrogen concentration and total ammonia-plus-organic (Kjeldahl) nitrogen concentration for NWQL samples. Prior to February 1996, total nitrogen was computed as the sum of dissolved nitrite-plus-nitrate nitrogen concentration and total Kjeldahl nitrogen concentration for VDCLS samples. Total phosphorous is computed as the sum of particulate phosphorous and dissolved phosphorous.

VIII. DATA REDUCTION, VALIDATION, AND REPORTING

Three VDCLS laboratory request forms - one each for filtered nutrients, total nutrients, and total solids analyses - are completed for each sample collected (Appendix 5). Field measurements of water temperature, air temperature, pH, specific conductance, barometric pressure, and dissolved oxygen are recorded for each sample collected. This information is recorded on both the Virginia District field form (Appendix 7) and on the VDCLS laboratory analytical services request form. When laboratory-split samples are collected, the NWQL analysis request form is also completed and sent with the samples to NWQL.

The USGS Virginia District field sheet that details field conditions and field parameter values is completed for each sampling trip and kept in the USGS Office along with a copy of the analytical services request forms. The field parameter values are entered into the Virginia District QWDATA water-quality data base at the office.

Selected quality-assurance analyses will be performed by the USGS laboratory in Denver, Colorado. The laboratory maintains its own rigorous quality control program and incorporates this information into a user-friendly quality-assurance data base. All laboratory data are reviewed by project personnel. The data are verified by comparing values with the ranges of values from prior samplings and by the review of data plots. If an error is found with the analysis, a re-run is requested, if within one month of sampling.

Water-quality analyses performed are stored on the Virginia District QWDATA water-quality data base. QWDATA is used to update the EPA data base STORET. Raw data are published in the USGS Annual Report for Virginia. The appropriate data originator is notified of errors so that the source data bases can be corrected and thus remain consistent with all others.

IX. INTERNAL QC CHECKS

A. Field

The quality assurance practices of field procedures include documentation of cross-section, depth-integrated variability; quality assurance of field personnel; documentation of field sampling status; and collection of field and laboratory blanks. These practices are described in greater detail in Section III.

B. Laboratory

<u>VDCLS</u>--The quality assurance practices of VDCLS including quality control, quality assurance of analytical results, quality assurance of all materials used in the preservation and containment of water-quality samples, and the blind- reference sample quality assurance program, are documented in *Quality Assurance Plan for the Virginia Division of Consolidated Laboratory Services*. Most analytical procedures used are referenced in *Chemical Analysis for Water and Wastes*: USEPA-600/4-79-020, Environmental Protection Agency, 1979, and *Standard Methods for the Examination of Water and Wastewater* (17th ed) edited by Clesceri et al., 1989.

<u>NWQL.</u>-- The quality assurance practices of NWQL are documented in the Techniques of Water Resources Investigations (TWRI) report entitled *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments*, Book 5, Chapter A6, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982. Included in this publication are: analytical methods development procedures; standard quantitative analysis techniques; instrumental techniques; laboratory quality control; quality assurance monitoring; documentation, summary, and evaluation of data; and material evaluation.

Analytical procedures and quality control of NWQL, including accuracy and precision statements, are documented in the TWRI report entitled *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, Book 5, Chapter A1, M.J. Fishman and L.C. Friedman, Open-file report 85-495, Denver, 1985.

Quality assurance of analytical results received from the participating laboratories incorporate both quality control and quality assurance monitoring. Quality-control monitoring is accomplished through the use of a personal and a computerized data review. Several computer checks are made which "flag" a possible error in analysis. These flags are documented on the analytical report specific to each sample. The completed analytical report is then reviewed by NWQL quality-assurance personnel prior to its release from the laboratory. The reviewers judge whether there is a reason for the data to have "failed" a check. If analytical error is suspected, a re-run of the sample is requested. Quality-assurance monitoring is also performed by the requestor of the analysis, whose familiarity with the site may allow them to identify an error that was not apparent to the laboratory personnel. If an error is found with the analysis, a re-run is requested.

Quality assurance of all materials used in the preservation and containment of water samples is performed by the USGS laboratory. Preservation materials, such as sulfuric acid, and sample bottles are randomly sampled by lot or batch number for any elevated trace metals and major cations and anions that may be present. If elevated levels are indeed found in either of these, the laboratory conducts additional sampling of the preservation materials and bottles, and if necessary, recalls them.

VDCLS and NWQL both participate in a nation-wide Standard-Reference Sample (SRS) quality-assurance program. This program was designed to evaluate the performance of each participating laboratory as well as monitor long-term trends in the bias and accuracy of analytical methodologies. Samples are prepared at the NWQL, Arvada, CO. Samples are prepared by the USGS Branch of Quality Assurance from which they are subsequently distributed to laboratories across the country. Results are published twice yearly and distributed to each participating laboratory and USGS Offices in each state.

X. PERFORMANCE AND SYSTEM AUDITS

Project reviews are conducted quarterly by USGS staff, and periodically by the USGS Area Water-Quality Specialist. USGS technical reviews are conducted periodically at the request of the principal investigator.

A District Water-Quality Review is held every three years by the USGS Regional Water-Quality Specialist and Regional Staff. Field methods are observed for consistency with national USGS procedures, and the District water-quality data base is examined for agreement between laboratory and field data. Checks are also done to ensure that the local water-quality data base, QWDATA, and the National data base, STORET, are in agreement.

The project officer and other staff from VaDEQ are kept informed of the status of the project on a quarterly basis by the development of a quarterly report detailing the number of samples collected per site and any problems associated with sampling or analysis.

Both VDCLS and NWQL participate in a Standard-Reference Sample quality-assurance program that analyzes the laboratory's performance as described previously.

XI. PREVENTIVE MAINTENANCE

Preventive maintenance of field instruments is done on a routine basis to ensure that the instruments remain in good working order. All potentially fragile electrodes and cells are stored in such a manner as to prevent breakage. Additionally, they are kept clean and free from any build-up that may affect their performance; rejuvenation of electrodes is performed periodically. All field meters and calibration standards are removed from vehicles and brought indoors after use to avoid mechanical or electronic problems caused by extremes in temperature. Batteries are changed and/or units recharged regularly.

All field instruments are calibrated prior to use, as described in Section VI, Calibration Procedures and Frequency. If an instrument is not in good working order, spare instruments are readily available so that there is no interference with field operations. Instruments in need of repair are repaired in a timely manner.

XII. ASSESSMENT OF DATA VARIABILITY, BIAS, ACCURACY, REPRESENTATIVE-NESS, AND COMPLETENESS

Assessment of data variability and bias for the Virginia River Input Monitoring Program consists of collecting and analyzing duplicate and laboratory-split samples. The purpose of these quality assurance practices is to quantify the variability of results from VDCLS, the major laboratory that provides analyses for this study, and to check for bias at VDCLS and NWQL. In addition, a Wilcoxon signed-rank test is used to evaluate differences in data results between laboratories.

Between 5 and 10 percent of the samples collected at each monitoring site are collected as duplicate samples. For each duplicate sampling, two unmarked duplicate samples labeled five minutes apart will be collected from the same churnsplitter and sent to VDCLS for the purpose of checking the analytical precision of the laboratory. Between 5 and 10 percent of the samples collected at each monitoring site are collected as laboratory-split samples. From a churnsplitter, one sample will be sent to the VDCLS for analysis and the other to NWQL for the purpose of verifying that these two laboratories are producing comparable results. Any statistical difference (p < 0.1) between the two laboratories is examined for possible sources of differences or analytical problems.

Field blanks analyzed by VDCLS are used to verify that clean sampling techniques are used by field personnel. Field blanks are collected by processing an analyte-free water through sampling equipment at the field site.

Periodically, standard-reference samples are submitted to VDCLS and the NWQL in order to check analytical results against a known standard. This allows for determination of the accuracy of each laboratory and the presence of any bias. Sources of reference samples may be either the Environmental Protection Agency or a commercial laboratory.

Completeness is assessed by comparing the number of base flow and stormflow samples completed with those scheduled. The reasons for any discrepancies are well documented.

XIII. CORRECTIVE ACTION FOR OUT-OF-CONTROL SITUATIONS

Out-of-control situations may occur in the field or in the laboratory as a result of equipment breakdown, despite careful planning and attention to procedures.

The primary methods for correcting out-of-control situations in the field are (1) repairing, recalibrating, or adjusting the malfunctioning instruments; or (2) substituting an alternative piece of equipment. Notes are made in the field log books and on the sampling field sheet when out-of-control situations occur. In most instances, no data are lost due to malfunctioning field equipment.

Potential out-of-control situations occurring in the laboratory may be identified by determining constituent concentrations that do not follow established concentration/discharge patterns or that seem out of range. The primary method of correcting out-of-control situations at VDCLS is to first re-examine the paperwork for clerical or translation errors, such as an incorrect date or station. The next step would be to examine the field paperwork to look for any written observations of problems at the site. Finally, if the source of the questionable value could not be discerned, the next step is to contact the laboratory to ask for confirmation of that concentration and to ask for any bench observations that might influence the sample concentrations. Based on the result of any of these steps, any mismatched site information and data would be corrected if possible. No data are ever changed unless there is a logical, fact-based reason for doing so. Any changes and the rationale for the changes are clearly documented on the District Field Sheet and initialed by the Project Chief or a senior project person.

XIV. QA REPORTING PROCEDURES

All samples collected at the five rivers will be analyzed at VDCLS in Richmond, VA. VDCLS performance will be evaluated through the use of duplicate and standard-reference samples. Results of the laboratory's performance will be documented with the quarterly reports, pending the receipt of analyses from the laboratory.

Interlaboratory performance is also evaluated using laboratory-split samples to compare analytical results from VDCLS and NWQL. These results are included in the quarterly report. Current evaluation of the quality-assurance data includes performing a Wilcoxon signed-rank test to determine statistical differences between laboratories. Findings are documented in the formal reports, and new procedures or quality-assurance tests are suggested when there is cause for question.

Additionally, interlaboratory performance is evaluated through a round-robin split sample program for several laboratories participating in the Chesapeake Bay monitoring program. This program is being conducted through the USGS Baltimore Office.

Selected References

- Clesceri, L.S., Greenberg, A.E., and Trussell, R.R., eds., 1989, Standard methods for the examination and treatment of water and wastewater (17th ed.), Washington, D.C., p. 2-1š, 5-82.
- Edwards, T.K., and Glysson, D.G., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments, U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 703 p.
- Helsel, D.R., and Cohn, T.A., 1988, Estimation of descriptive statistics for multiply censored water quality data: Water Resources Research, v. 24, no. 12, p. 1997-2004.
- Horowitz, A.J., C.R. Demas, K.K. Fitzgerald, T.L. Miller, and D.A. Rickert, 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.
- Pettyjohn, W.A., and Henning, R., 1979, Preliminary estimate of ground-water recharge rates, related streamflow and water quality in Ohio: The Ohio State University Department of Geology and Mineralogy Completion Report No. 522, 323 p.
- Ward, J.R., and Harr, Albert, 1990, Methods for collection and processing of surface-water and bedmaterial samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.
- White, K.E., and Sloto, R.A., 1990, Base-flow-frequency characteristics of selected Pennsylvania streams: U.S. Geological Survey Water Resources Investigation Report 90-4160, 67 p.

APPENDIX 1. CRITERIA FOR STORMFLOW SAMPLING

Stream gages upstream of selected monitoring stations and at some monitoring stations were outfitted with telemetry equipment, to monitor water-level changes as a result of precipitation in order to help determine when to collect stream samples. Telemetry equipment could not be installed at the Rappahannock River station near Fredericksburg because of the remoteness of the site. Decisions, therefore, about sampling criteria were based on the flow conditions at the two telemetry stations upstream, the Rappahannock River near Remington and the Rapidan River near Culpeper. The Rappahannock River station near Fredericksburg was inaccessible during extreme high-flow events; therefore, stormflow samples were collected at those times from the Interstate-95 (I-95) bridge about one mile downstream of the stream gage. There are no major contributors of flow to the river between the two sites.

Table A1.Criteria for storm flow sam pling at Jam es Rivernear Cartersville (020305000) [>, greater than; <, less than; ft^3/s , cubic feet per second; ft, foot]

Gage height (ft)	Mean daily flow (ft ³ /s)	Flow duration (percent of time indicated discharge was equaled or exceeded)	Sampling frequency (percent)		
>17.7	>58,000	<2	100		
14.2-17.7	40,000-58,000	2-5	<u>a</u> />90		
6- 14.2	12,000-40,000	5-17	<u>b/</u> 50-100		
<6	<12,000	17-100	<u>c</u> ∕13		

 $[\]underline{a}$ /Attempt to sample >90 percent of days with streamflows in excess of 21,000 ft³/s.

 $[\]underline{b}'$ The percentage will differ depending on weather conditions. During dry periods, attempts were made to sample all days in this streamflow range; during wet periods, attempts were made to sample on at least half the days when streamflow was in this range.

 $[\]underline{c}'$ The percentage is based on the 24 base-flow samples scheduled per year (by the U.S. Geological Survey). However, during extreme dry periods, this sampling frequency could be increased to include small precipitation events to estimate loads more accurately.

Table A 2.C riteria for storm flow sam pling at Rappahannock Rivernear Fredericksburg (01668000) [>, greater than; <, less than; ft^3/s , cubic foot per second; ft, foot]

Gage height (ft)	Mean daily flow at the Fredericksburg gage (ft ³ /s)	Flow duration (percent)	Sampling frequency (percent)		
> 6.7	> 9,800	< 2	<u>a</u> /100		
6.1-6.7	7,500-9,800	2-5	<u>b/</u> >90		
3.7-6.1	2,000-7,500	5-35	<u>c</u> /50-100		
<3.7	< 2,000	35-100	₫/13		

 $[\]frac{a}{S}$ Sample from the Interstate-95 bridge when the gage height exceeds 12 feet. Location change recorded on field sheet.

Table A3.Criteria for storm flow sam pling at Appom attox R iveratM atoaca (02041650) [>, greater than; <, less than; ft^3/s , cubic feet per second; ft, foot]

Gage height (ft)	Mean daily flow (ft ³ /s)	Flow duration (percent)	Sampling frequency (percent)		
>9.7	>9,800	<2	100		
8.6-9.7	7,900-9,800	2- 5	<u>a</u> />90		
4.5-8.6	1,900-7,900	5- 30	<u>b/</u> 50-100		
<4.5	<1,900	30-100	<u>c</u> /13		

^a/Attempt to sample all days with streamflows in excess of 5,700 ft³/s.

 $[\]underline{b}'$ Attempts were made to sample on >90 percent of days when streamflow was in excess of 5,000 ft³/s at the Fredericksburg gage (or 3,800 ft³/s combined flow of gages on Rappahannock River at Remington, Va., and Rapidan River near Culpeper, Va.).

^{c/}The percentage will differ depending on weather conditions. During dry periods, attempts were made to sample on all days when streamflow was in this range; during wet periods, attempts were made to sample on at least half the days when streamflow was in this range.

d/The percentage is based on the 24 base-flow samples scheduled per year (by the U.S. Geological Survey). However, during extreme dry periods, this sampling frequency could be increased to include small precipitation events to improve load estimations.

 $[\]underline{b}$ The percentage will differ depending on weather conditions. During dry periods, attempt to sample all days in this streamflow range; during wet periods, attempt to sample at least half the days in this streamflow range.

c/The percentage is based on the 24 base-flow samples scheduled per year (by the U.S. Geological Survey). However, during extreme dry periods, this sampling frequency could be increased to include small precipitation events to improve load estimates.

Table A 4. Criteria for storm flow sam pling at Pam unkey R ivernear Hanover (01673000) [>, greater than; <, less than; ft^3/s , cubic feet per second; ft, foot]

Gage height (ft)	Mean daily flow (ft ³ /s)	Flow duration (percent)	Sampling frequency (percent)
>19.5	>8,000	<2	100
17-19.5	6,000-8,000	2- 5	<u>a</u> />90
8-17	1,500-6,000	5- 25	<u>b/</u> 50-100
<8	<1,500	25-100	<u>c</u> /13

 $[\]underline{a}$ /Attempts were made to sample on >90 percent of days when streamflow was in excess of 4,500 ft³/s.

Table A5.Criteria for storm flow sam pling at MattaponiR ivernear Beulahville (01674500) [>, greater than; <, less than; f^3/s , cubic feet per second; ft, foot]

Gage height (ft)	Mean daily flow (ft ³ /s)	Flow duration (percent)	Sampling frequency (percent)
>16.5	>4,900	<2	100
14.7-16.5	3,300-4,900	2-5	<u>a/</u> >90
6-14.7	520-3,300	5- 60	<u>b</u> /50-100
<6	<520	60-100	<u>c</u> /13

^a/Attempts were made to sample on >90 percent of days when streamflow was in excess of 1,700 ft³/s.

 $[\]underline{b}'$ The percentage will differ depending on weather conditions. During dry periods, attempts were made to sample all days when streamflow was in this range; during wet periods, attempts were made to sample on at least half the days when streamflow was in this range.

^CThe percentage is based on the 24 base-flow samples scheduled per year (by the U.S. Geological Survey). During extreme dry periods, however, this sampling frequency could be increased to include small precipitation events to estimate loads more accurately.

b/The percentage will differ depending on weather conditions. During dry periods, attempts were made to sample on all days when streamflow was in this range; during wet periods, attempts were made to sample on at least half the days in this streamflow range.

 $[\]underline{c}'$ The percentage is based on the 24 base-flow samples scheduled per year (by the U.S. Geological Survey). However, during extreme dry periods, this sampling frequency could be increased to include small precipitation events to improve load estimates.

APPENDIX 2 - EXAMPLE OF FIELD DATA RECORD

	B F 0	B F 0 2	B F 0 3	B F 0 4	B F 0 5	B F 0 6	F B L K	B F 0 7	B F 0 8	B F 0 9	B F 1	B F 1	B F 1	D U P L b	B F 1	B F 1	B F 1	B F 1	B F 1	B F 1	S P L T C	B F 1	B F 2	B F 2	B F 2	B F 2	B F 2 4	
GET EXTRA SAMPLES																												
Gage Height																												
Scheduled Date																												
Sam pled Date																												
Personnel																												
Lab Sheet to PI																												
Databack from State																												
Entered into QW DATA																												
Cursory Check																												
Q A check																												
Problem s																												
Problems solved																												
QtrRpt																												

46

APPENDIX 3 -- CRITERIA FOR EQUIPMENT USE

Table A6.C riteria for equipm entuse during storm flow and base-flow sampling at James Rivernear Cartersville (02035000)

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<2.5	Weighted bottle	NA	2
2.5-12	D-74AL	3/16	1
12 -19	D-74	1/8	1
>19	D-74 + 50 pounds	1/8	1

Table A7.C riteria for equipm entuse during storm flow and base-flow sampling at Rappahannock Rivernear Fredericksburg (01668000)

[Above a gage height of 12 feet, the cableway is unsafe to operate, and sampling should be done from the I-95 bridge. Five equally-spaced depth-integrated samples will be collected. NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<5	Weighted bottle	NA	2
5- 9	D-74AL	3/16	1
9-12	D-74	3/16	1
>12	D-74	1/8	1

Appendix 3.(continued) Criteria for Equipment Use

Table A 8.C riteria for equipm entuse during storm flow and base-flow sampling at Appom attox R iver at M atoaca (02041650) [NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<3.5	Weighted bottle	NA	2
3.5 - 7.5	D-74AL	3/16	1
7.5 - 11	D-74	1/8	1
>11	D-74 + 50 pounds	1/8	NA

Table A 9 Criteria for equipm entuse during storm flow and base-flow sampling at Pam unkey R ivernear Hanover (01673000)

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<9	Weighted bottle	NA	2
9 - 20	D-74AL	3/16	1
>20	D-74	3/16	1

 $\label{thm:lower} \textbf{Table A10.Criteria for equipm entuse during storm flow and base-flow sampling at \texttt{MattaponiR}\ ivernear\ \texttt{Beulahville}\ (01674500)$

[NA, not applicable]

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<11	Weighted bottle	NA	2
11- 17	D-74AL	3/16	1
>17	D-74	1/8	1

APPENDIX 4 FIELD SAMPLING PROCEDURES

RIVER INPUT MONITORING PROCEDURES AT JAMES RIVER NEAR CARTERSVILLE (02035000)

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; field meters and standards (dissolved oxygen, conductance, p1ECH); D.O. probe with calibrating chamber; 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters and pump.

PAPERWORK: 3 VDCLS Field Sheets (1 unfiltered nutrients, 1 filtered nutrients, 1 nonmetals [solids]); Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

- 2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.
- 3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the D-74 or D-74AL (use only the nylon nozzles), have wire cutters with you at each station on the bridge. If using a YSI dissolved oxygen meter, let stabilize for 20 minutes, calibrate, and then lower probe into the mid-point of the water column to let it equilibrate to the water temperature.
- 4. Calibrate pH and conductance meters, recording calibrations on the field sheets and noting any problems.
- 5. Collect five depth-integrated subsamples from the Cartersville Bridge and composite in the churnsplitter.

Subsamples will be collected from the centroids of five equal-discharge river increments. The table below details the sampling locations at the foot markings on the bridge at various stages.

Gage height (ft)	Sampling locations (ft)
All gage heights	260, 380, 500, 620, 740

Depth-integrating sampling equipment is used to collect samples when the mean stream velocity exceeds 1.5 f/s, which corresponds to a gage height of about 2.5 feet. When the gage height is below 2.5 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. The table below summarizes the equipment needs for sampling at various river stages.

Gage height (ft)	Sampler	Nozzle (inch)
<2.5	Weighted bottle	NA
2.5 - 12	D-74AL	3/16
12 - 19	D-74	1/8
19 - 32	Point sampler	1/8

Minimum amount of water to collect during routine sampling:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	3 glass bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	4 glass bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle "Duplicate" on Virginia District field sheet, and enter the respective times.

- 6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid.
- 7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences $^{\$}$ 0.45 μ m polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered water, then fill.

- 8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.
- 9. After samples have been collected from the churnsplitter, measure (in the order listed): temperature, conductance, pH, barometric pressure, air temperature, and dissolved oxygen. All parameters other than D.O. may be taken from the churnsplitter. Single-point D.O. measurements will be taken in-situ after the equilibration described in step 3. Please note on the field sheet the water quality instruments used and the serial numbers. Fill out state lab sheets.
- 10. Clean and store instruments and equipment. Pick up any safety cones.
- 11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.
- 12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.).

RIVER INPUT MONITORING PROCEDURES AT

RAPPAHANNOCK RIVER NEAR FREDERICKSBURG (01668000)

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; field meters and standards (dissolved oxygen, conductance, pH); D.O. probe with calibrating chamber; 3 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters, and pump.

PAPERWORK: 4 VDCLS Field Sheets (1 unfiltered nutrients, 1 filtered nutrients, 1 nonmetals [solids]); Virginia District Field Sheet

If quality assurance samples are to be taken, take extra lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

- 2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Inspect the tape, noting time, dial reading, and inside gage reading. If using a YSI dissolved oxygen meter, let stabilize for approximately 20 minutes, calibrate, and then lower probe into mid-point of the water column to let it equilibrate to the water temperature.
- 3. Calibrate pH and conductance meters, recording calibrations on the field sheets and noting any problems.
- 4. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the D-74 or D-74AL (use only the nylon nozzles), the following equipment is required: wire cutters, gloves, cable pullers, life vest, spare nylon nozzles, flat-head screwdriver, sampler pin, cleaned and bagged churnsplitter, and cleaned and bagged glass bottle. If using the weighted bottle sampler, you will need: rope, cleaned and bagged churnsplitter, cleaned and bagged sample bottle, and cable pullers. Put on life vest. Inspect the cableway and surrounding area for damage before climbing the tower and entering the cart.
- 5. Make sure the brake is on before unlocking the locks. Take the brake off, continue to hold the brake rod, and ride to the left bank. Use the cable pullers to slow the cart until reaching the first sampling point. Be alert for submerged logs. If the sampler cable becomes snagged, let all the line out and quickly cut the line.
- 6. Collect water five depth-integrated subsamples from the cableway and composite in the churnsplitter. Subsamples will be collected from the centroids of five equal-discharge river increments. The table below details the sampling locations at the markings on the cableway at various stages.

Gage height (ft)	Sampling locations (ft)	
All gage heights	90,170, 270, 340, 420	

Above a gage height of 12 feet, the cableway is unusable. Sampling from the I-95 bridge at Fredericksburg will be undertaken using a 150 foot cable. Subsamples will be collected at the center of five equal-width-increment sections. The width of the increments to be sampled is determined by dividing the stream width by 5 (number of verticals).

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 f/s, which corresponds to a gage height of about 5 feet. When the gage height is below 5 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. Five equally-spaced depth integrated samples will be collected. The table below summarizes the equipment needs for sampling at various river stages.

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
< 5	Weighted bottle	NA	2
5 - 9	D-74AL	3/16	1
9 - 12	D-74	3/16	1
> 12	D-74	1/8	1

Minimum amount of water to collect during routine sampling.:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	3 glass bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water	
Weighted bottle	1 bottle at each station	
D-74 or D-74 Al	4 glass bottles at each station	

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle "Duplicate" on Virginia District field sheet, and enter the respective times.

- 7. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid.
- 8. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences $^{\circledR}$ 0.45 μ m polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered sample, then fill.

- 9. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.
- 10. After samples have been collected from the churnsplitter, measure (in the order listed): temperature, conductance, pH, barometric pressure, air temperature and dissolved oxygen. All parameters other than D.O. may be taken from the churnsplitter. Single-point D.O. measurements will be taken in-situ after the equilibration described in step 3. Please note on the field sheet the water quality instruments used and the serial numbers. Fill out state lab sheets.
- 11. Clean and store instruments and equipment. Pick up any safety cones.
- 12. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the tape on the ADR. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.
- 13. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab. Write any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems).

RIVER INPUT MONITORING PROCEDURES AT APPOMATTOX RIVER AT MATOACA (02041650)

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; field meters and standards (dissolved oxygen, conductance, pH); D.O. probe with calibrating chamber; 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters, and pump.

PAPERWORK: 3 VDCLS Field Sheets (1 unfiltered nutrients, 1 filtered nutrients, 1 nonmetals [solids]); Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

- 2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.
- 3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the D-74 or D-74AL (use only the nylon nozzles), have wire cutters with you at each station on the bridge. If using a YSI dissolved oxygen meter, let stabilize for 20 minutes, calibrate, and then lower probe into mid-point of water column to let it equilibrate to the water temperature.
- 4. Calibrate pH and conductance meters, recording calibrations on the field sheets and noting any problems.
- 5. Collect four depth-integrated subsamples from the Matoaca Bridge and composite in the churnsplitter.

Subsamples will be collected from the centroids of four equal-discharge river increments corresponding to 12.5%, 37.5%, 62.5% and 87.5% of the cumulative flow. The table below details the sampling locations at the foot markings on the bridge at various stages.

Gage height (ft)	Sampling locations (ft)
<12	140, 195, 240, 295
>12	120, 180, 240, 295

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 ft/s, which corresponds to a gage height of about 3.5 feet. When the gage height is below 3.5 feet, samples are collected using a weighted bottle. The depth-integrating sampler is not effective at low velocities. The table below summarizes the equipment needs for sampling at various river stages.

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
< 3.5	Weighted bottle	NA	2
3.5 - 7.5	D-74AL	3/16	1
7.5 - 11	D-74	1/8	1
> 11	D-74 + 50 pounds	1/8	NA

Minimum amount of water to collect during routine sampling:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	3 glass bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	4 glass bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle "Duplicate" on Virginia District field sheet, and enter the respective times.

- 6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid.
- 7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences $^{\circledR}$ 0.45 μ m polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered sample, then fill.

- 8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.
- 9. After samples have been collected from the churnsplitter, measure (in the order listed): temperature, conductance, pH, barometric pressure, air temperature and dissolved oxygen. All parameters other than D.O. may be taken from the churnsplitter. Single-point D.O. measurements will be taken in-situ after the equilibration described in step 3. Please note on the field sheet the water quality instruments used and the serial numbers. Fill out state lab sheets.
- 10. Clean and store instruments and equipment. Pick up any safety cones.
- 11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.
- 12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.).

RIVER INPUT MONITORING PROCEDURES AT PAMUNKEY RIVER NEAR HANOVER (01673000)

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; field meters and standards (dissolved oxygen, conductance, pH); D.O. probe with calibrating chamber; 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters, and pump.

PAPERWORK: 3 VDCLS Field Sheets (1 unfiltered nutrients, 1 filtered nutrients, 1 nonmetals [solids]); Virginia District Field Sheet

If quality assurance samples are to be taken, take extra cubitainers, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

- 2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.
- 3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the D-74 or D-74AL (use only the nylon nozzles), have wire cutters with you at each station on the bridge. If using a YSI dissolved oxygen meter, let stabilize for 20 minutes, calibrate, and then lower probe into mid-point of water column to let it equilibrate to the water temperature.
- 4. Calibrate pH and conductance meters, recording calibrations on the field sheets and noting any problems.
- 5. Collect five depth-integrated subsamples from the Hanover Bridge and composite in the churnsplitter.

Subsamples will be collected at the center of five equal-width-increment sections. The width of the increments to be sampled is determined by dividing the stream width by 5 (number of verticals). The equal-width-increment method is used at this site because the streambed, and therefore distribution of water discharge in the cross section, is not stable.

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 ft/s, which corresponds to a gage height of 9.0 feet. When the gage height is below 9.0 feet, grab samples will be collected with a weighted bottle sampler from the five determined locations. The table below summarizes the equipment needs for sampling at various river stages.

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<9	Weighted bottle	NA	2
9 - 20	D-74AL	3/16	1
>20	D-74	3/16	1

Minimum amount of water to collect during routine sampling:

Sampler Amount of water	
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	3 glass bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	4 glass bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle "Duplicate" on Virginia District field sheet, and enter the respective times.

- 6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid.
- 7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences $^{\circledR}$ 0.45 μ m polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered sample, then fill.
- 8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.
- 9. After samples have been collected from the churnsplitter, measure (in the order listed): temperature, conductance, pH, barometric pressure, air temperature and dissolved oxygen. All parameters other than D.O. may be taken from the churnsplitter. Single-point D.O. measurements will be taken in-situ after the equilibration described in step 3. Please note on the field sheet the water quality instruments used and the serial numbers. Fill out state lab sheets.
- 10. Clean and store instruments and equipment. Pick up any safety cones.
- 11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.

12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.).

RIVER INPUT MONITORING PROCEDURES AT

MATTAPONI RIVER NEAR BEULAHVILLE (01674500)

Please complete the following tasks in the order they are listed.

1. Look at the sampling schedule in the QW Area and determine if a quality assurance sample is scheduled. If no extra samples are to be taken, the following items are required:

EQUIPMENT: Cooler with approx. 5" of ice; cleaned and bagged churnsplitter; cleaned and bagged glass sampling bottle for sampler; field meters and standards (dissolved oxygen, conductance, pH); D.O. probe with calibrating chamber; 4 cubitainers, plus at least 1 extra; VDCLS labels; tubing, filters, and pump.

PAPERWORK: 3 VDCLS Field Sheets (1 unfiltered nutrients, 1 filtered nutrients, 1 nonmetals [solids]); Virginia District Field Sheet.

If quality assurance samples are to be taken, take extra cubitainers, VDCLS lab sheets and USGS lab sheets. All necessary forms are in the River Input folders in the lab.

- 2. Upon arrival at the site, read the gage height and note if the level is rising or falling. Note time, dial reading, and inside gage reading. Set out safety cones and put on safety vest.
- 3. Set up sampling equipment. Refer to sampler protocol sheet to determine which sampler should be used. If using the D-74 or D-74AL (use only the nylon nozzles), have wire cutters with you at each station on the bridge. If using a YSI dissolved oxygen meter, let stabilize for 20 minutes, calibrate, and then lower probe into mid-point of water column to let it equilibrate to the water temperature.
- 4. Calibrate pH and conductance meters, recording calibrations on the field sheets and noting any problems.
- 5. Collect four depth-integrated subsamples from the Beulahville bridge and composite in the churnsplitter.

Subsamples will be collected from the centroids of four equal-discharge river increments. The table below details the sampling locations at the foot markings on the bridge at various stages.

Gage height (ft)	Sampling locations (ft)
<6	85, 73, 65, 53
6 - 12	91, 77, 65, 53
>12	100, 72, 58, 40

Depth-integrating sampling equipment will be used to collect samples when the mean stream velocity exceeds 1.5 ft/s, which corresponds to a gage height of about 11 feet. When the gage height is below 11 feet, samples are collected using a

weighted bottle. The depth-integrating sampler is not effective at low velocities. The table below summarizes the equipment needs for sampling at various river stages.:

Gage height (ft)	Sampler	Nozzle (inch)	Bottle (liter)
<11	Weighted bottle	NA	2
11 - 17	D-74AL	3/16	1
>17	D-74	1/8	1

Minimum amount of water to collect during routine sampling

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	3 glass bottles at each station

Minimum amount of water to collect when doing duplicates or lab splits:

Sampler	Amount of water
Weighted bottle	1 bottle at each station
D-74 or D-74 Al	4 glass bottles at each station

The time of sample will be the temporal mid-point of sampling. If collecting a sample for VDCLS only, label the sample on quarter hours.

Duplicates should be labeled 15 minutes after the regular samples (i.e., 1200 for the first set of samples and 1215 for the second set of samples). Circle "Duplicate" on Virginia District field sheet, and enter the respective times.

- 6. To process the unfiltered samples, sample-rinse cubitainers thoroughly, then fill. Churn continuously without breaking the water surface while filling. If collecting lab split to be sent to NWQL, preserve with 1 mL 4.5N sulfuric acid. Wear latex gloves when working with sulfuric acid.
- 7. To process the filtered samples, first connect the tubing to the pump, and then connect the filter (Gelman Sciences $^{\circledR}$ 0.45 μ m polysulfone filter) to the end of the tubing. Run approximately 500 mL of sample through the tubing and filter to sample-rinse. Next, sample-rinse the cubitainers thoroughly with filtered sample, then fill.
- 8. Fill out labels with appropriate times as described above, and place samples in ice. All shaded boxes on laboratory forms are REQUIRED and MUST match the information on the label for each sample.

- 9. After samples have been collected from the churnsplitter, measure (in the order listed): temperature, conductance, pH, barometric pressure, air temperature and dissolved oxygen. All parameters other than D.O. may be taken from the churnsplitter. Single-point D.O. measurements will be taken in-situ after the equilibration described in step 3. Please note on the field sheet the water quality instruments used and the serial numbers. Fill out state lab sheets.
- 10. Clean and store instruments and equipment. Pick up any safety cones.
- 11. Return to gage house and record gage height reading. Note on the field sheet if the level was rising or falling by reading the CR10 interface. If the level changed significantly during sample, record the gage height that was taken closest to the time put on the sample labels.
- 12. Take samples to Virginia Division of Consolidated Labs (VDCLS). If samples were taken on the weekend or late in the afternoon, put samples in USGS District lab refrigerator. Write down any sampling problems or observations on the USGS field sheet (i.e., river especially muddy, meter calibration problems and how fixed, other equipment problems. ANY information can sometimes help.).

APPENDIX 5 -- VIRGINIA DIVISION OF CONSOLIDATED LABORATORY SERVICES ANALYTICAL REQUEST FORMS

VIRGINIA DEPARTMENT OF ENVIRONMENTAL QUALITY DCLS LAB USE ONLY

_ PROG.CODE STATIO	ON ID	DATE COLLECTED	TIME COLLECTED	M/F SURVEY	DEPTH	
		YYMMI) D			
_ CATALOG NUMBER	GROUP	CODE PRIORITY C	ODE CONTAINER#	UNIT CODE R	EGION CODE CO	LLECTOR
SPECIAL STUDY NUMBER	ER %FRB	WEATHER TIDE	FLOW SEVERITY	SECCHI DEPTH(m)	FIELD pH	
						_
00116	00002	2 00041 00	0067 01351	00078	0040	0
RESIDUAL CHLORINE	FLOW RATE	COLLECTION SPA	AN # OF ALIQUOTS	AIR TEMP.(Co)	BAROMETER PR	ESSURE
						-
50060	00061			00	020	00025
_ SWL	SPWL	HOURS	YIELD			
_G						
_ w						
TIGOTIA	DECIEGANDO	CAMPLE NO	THE (ALDILA)	CDECTEC(ALDUA)		
_T		SAMPLE NO.	TIS(ALPHA)	SPECIES(ALPHA)	1	
_ I						
74995 _ S _	74990		84007	84005	5	
IND/SAMPLE	SEX	LENGTH(INCHES)	_ WEIGHT(LBS)	LC/H		
 _ U					_	
	84014	00024	00023	84008		
LATITUDE		D.O.PROBE(m	g/l) _ TEMP(C) _ CO	ND.(uMHOS/CM) _	SALINITY(ppt) _	
LONGITUDE		00299	00010	00094	00096	
OTHER						
COUNTY	_					
COMMENTS						

APPENDIX 6 -- U.S. GEOLOGICIAL SURVEY - NATIONAL WATER-QUALITY LABORATORY ANALYTICAL SERVICES REQUEST FORM

				SAMPLE
SMS CONTROL NO	NWIS RECORD N	O LABO	DRATORY ID	SET
STATION	N NAME			
FIELD OFFICE	*PHONE NO.	*PROJECT CHIEF	FIELD SAMPLE ID	SITE TYPE
*STATE	*DISTRICT/USER	CNTY	*PROJECT ACCT NO	
BEG	IN DATE:			
END	DATE: YEAR MONTH	DAY TIME		
	SCHEDULES, FIELD A		CODES	
SCHEDULE 1:		EDIUM:	**SAMPLE TYPE:	
SCHEDULE 2:		C UNIT:		
SCHEDULE 3:		TATUS:	**HYDRO EVENT:_	
SCHEDULE 4:		OURCE:		
SCHEDULE 5:		DITION:		
A/D	A/D	A/D	A/D	
CODE:		CODE:	CODE:	
CODE:		CODE:	CODE:	_
CODE:	•	CODE:	CODE:	_
CODE:	CODE:	CODE: _	CODE:	_
	FIELD	VALUES —		
LAB/P CODE VALUE RMK		E VALUE RMK	LAB/P CODE VALUE	RMK
21/ 00095	51/ 00400 _		64/_00010	
	/		/	
/	/ _			
+COMMENTS: (LIMIT TO	138 CHARACTERS):			
LOGIN COMMENTS:				
SHIPPED BY:		IONE:	DATE: _	
	BOTTLE TYPES (PLEAS	SE FILL IN NO. OF	TYPES SENT)	•
FARU	FUFAM		RCCFCCFAB	CU
RARAHVOA CHY	SCN- O&GPHENO	RCB L WCA	DOCTOCSOC	COD
	E APPROVED BY:		AL NO	
PROGRAM/PROJECT:N			ING H20 FILL IN OTHER	
POSSIBLE HAZARDS		65DKITYK		
		0.5		

APPENDIX 7 -- VIRGINIA DISTRICT RIVER INPUT MONITORING FIELD SHEET

U S . G E O L O G ICAL SURVEY , W RD , SURFACE W ATER QUALITY FIELD NOTES

ProjName:	FALL LINE MONITORING	Projectno.	44510030)1 Date_	Tim e
Station nam e	Rappahannock Rivernr Frede	ricksburg	Sta.No.	01668000	Sam pled by

SAMPLE TYPES AND QUALITY ASSURANCE (*Forothers, check full list of QA codes.) FIELD MEASUREMENTS

*LabelVDCLS replicates 15 m inutes pastregular sam ples,NW QL lab splits 5 m inutes pastregular sam ples, and blanks 5 m inutes before regular sam ples.							
SampleType *Time Medium Sample DuplType Analyzing Lab Type 99105 00028							
Regular	gular 9 9 85116						
Replicate		R	7	30 (split)	85116		
Lab Split R 7 200 (lab-split) 80020							
B lank Q 2 85116 /80020							
Reference Q 6 85116 /80020							
0 ther							

M easurem ent	Value	Units
Q. Inst. (00061)		cfs,determ ined by: meas. rating est.
Gage Ht. (00065)		feet [@]
Tem p.W ater (00010)		deg C
Tem p.Air (00020)		deg.C
Sp.Cond.(00095)		uS/cm 25 deg
рн (00400)		units
Dis Oxy. (00300)		mg/L
Bar.Press (00025)		mm Hg

Analysis status H initial entry

Analysis source G USGS felt and non-USGS lab 9 USGS lab and felt

<u>Hydrologic conditions</u> A NotDetermined 4 Stable, bw 5 Falling 6 Stable, high 7 Peak 8 Rising 9 Stable, normal <u>Hydrologic event (severity)</u> 9(3) Routine sample J(4) Storm 1(2) Drought 2 Spill 3 Regulated flow 4 Snowmelt 7 Fbod

SAMPLING CONDITIONS

Hot Other_____

Sam pler type 84164: 3009-D74 (brass, 60 bs.) 3	3010-D74-AL (Aluminum, 35 bs)	3060-Weighted Bottle/Frame	8010-0 ther
---	----------------------------------	----------------------------	-------------

Sam pling Method 82398: 10 EW I 20 EDI other	Nozzle sizeinch,made of
Sampling Points: standard 90 170 270 340 420	other
Stream Color(s) brown green blue gray other	_Stream Mixing: Clear/Turbid
W eather: Clear Partly Cloudy Cloudy Light Medium Heavy	Snow Rain Calm Light Breeze Gusty Windy Cold Cool Wa:

QUALITY ASSURANCE SAMPLES

Blanks Only (circle one in each column)					Reference Sam ples Only			
*Type Solution 99100		*Source 99101		*Type ofblank 99102		*R eference source 99103		Code no. (from source) 99104
code	Туре	code	sources	code	Sample	code	sources	code
10	Distilled/DI	10	NWQL	40	sampler	10	NWQL	
40	0 rganicfree	20	EPA	50	splitter	20	EPA	
200	0 ther	60	D ist. Lab	60	filter	60	D ist. Lab	
		80	0 cala	100	field eq.	80	0 cala	
				150	ab bank		0 ther	

FELD CALBRATION AND MEASUREMENTS

	PERATURE erature from:	M u l apar	am eterunit D(O Meter Them	om eter 0 ther			
			Date of AST	M checkonmeter	them isterorthem om	eter:		
					W ATER TEMPE	RATURE=	-	
pH Meter W -no			M eterM ake	eModel	electrode no .		electrode type	
	pH buffer buffer Initial reading temp		In it is lineading	Adjæading	R em arks	3	pH m easurem ents (3 required)	
	:							
_	bsample from calavg of	_		: Chum de point ats	Sample bottle stadepth		deg C eck date	
SDEC	CIFIC CONDU	ста ис	F.		MEDIAN PH=_			
Meter	W mo		MeterMa					
	Standard value	Std. temp*	In it is lineading	Adjæading	R em arks		Conductance Measurements (3 required)	
				<u> </u>				
					nple bottle stadepth		deg C ck date	
ם של ע	OLVED OXYO	2 FN			MEDIAN CONI	OUCTANCE=		
Vertic	alavg of Zero Check Y	_points		tatsta	depth x-se		points eck date	
BAR	.PRESS	m	m Hg WaterTe	em p	deg C .			
	MeterW-noMeterDO.Satmg/L MeterDO.Sat				Sat	Adjusted to)	
YS 185/95: Meter serialno. Calibrati				Calibrat	tion Value	%	Saturation	
			ENTRATION=					
0 the	r O bservatio	ns and R	em arks:					